A significant CO_2 sink in the tropical Atlantic Ocean associated with the Amazon River plume

Arne Körtzinger

Institut für Meereskunde, Universität Kiel, Kiel, Germany

Received 15 October 2003; accepted 19 November 2003; published 27 December 2003.

[1] During Meteor cruise 55 a strong undersaturation of surface seawater with respect to atmospheric CO_2 was found in the Amazon River plume which is advected into the surface circulation of the tropical Atlantic. A conservative estimate of the plume-related CO_2 sink in the tropical Atlantic yields a net air-sea flux of 0.014 ± 0.005 Pg C yr^{-1}. The corresponding average CO_2 flux density of 1.35 mmol m^{-2} d^{-1} is of similar magnitude but opposite sign as found elsewhere in the slightly supersaturated tropical Atlantic illustrating the significant impact of the Amazon on the biogeochemistry of large ocean areas. The dramatic change of the CO_2 saturation state from highly supersaturated river waters to markedly undersaturated surface waters in the plume can be explained by a combination of the effects of CO_2 outgassing from river water, of mixing between river and ocean water on the CO_2 system properties, and of strong biological carbon drawdown in the plume. *INDEX TERMS:* 4806 Oceanography: Biological and Chemical: Carbon cycling; 4235 Oceanography: General: Estuarine processes; 4271 Oceanography: General: Physical and chemical properties of seawater. **Citation:** Körtzinger, A., A significant CO_2 sink in the tropical Atlantic Ocean associated with the Amazon River plume, *Geophys. Res. Lett.*, *30*(24), 2287, doi:10.1029/2003GL018841, 2003.

1. Introduction

[2] Recognizing its important role in the anthropogenically perturbed earth system, the marine carbon cycle has been under steadily increasing scientific scrutiny during the last decades. The global surface ocean pCO_2 climatology by *Takahashi et al.* [2002] is a very good example of a synthesis product based on 940,000 pCO_2 measurements made over more than 40 years. Such products provide valuable insight into the CO_2 source and sink patterns of the world ocean. Due to the coarse resolution of the pCO_2 climatology and the lack of ancillary data it is often hard to interpret these patterns in terms of driving forces on a local scale. This is especially true for the influence of marginal seas and rivers on the observed pCO_2 patterns.

[3] Rivers can have a significant impact on the hydrography and biogeochemistry of large ocean areas. This is especially true for the Amazon River, by a considerable margin the largest river in the world. Like in most aquatic ecosystems, respiration exceeds autochthonous gross primary production in the Amazon. The resulting negative net ecosystem production is fueled by (particulate and dissolved) organic carbon leaking from the terrestrial system and causing the Amazon, like most rivers, to be highly supersaturated in CO_2 [*Cole and Caraco*, 2001]. The mainstem Amazon near Manaus is 10- to 20-fold supersaturated with lowest values occurring at falling water towards the end of the year [*Richey et al.*, 2002].

[4] When reaching the ocean, Amazon waters become increasingly less super- and eventually undersaturated with respect to atmospheric CO_2 by two major effects: (1) Strong shift in chemical CO_2 system equilibria due to mixing of river with high-alkalinity ocean waters [*Ternon et al.*, 2000], and (2), onset of diatom blooms due to rapid settling of river-borne suspended particles allowing waters to become sufficiently transparent for photosynthesis [*Edmond et al.*, 1981]. The henceforth undersaturated plume of the Amazon River is advected from the Brazilian coast into the intense North Brazil Current (NBC) which partly retroflects into the North Equatorial Countercurrent (NECC) and regularly sheds warm-core NBC rings translating on a trajectory parallel to the coastline towards the Caribbean [*Fratantoni and Glickson*, 2002]. This provides a mechanism for spreading the biogeochemical signatures of the Amazon River discharge into a large area of the tropical North Atlantic Ocean as can be seen in SeaWIFS ocean color images.

2. Measurement and Flux Calculation Methods

[5] The fugacity of CO_2 (fCO_2) in surface seawater and air was measured continuously along the cruise track of R/V Meteor cruise 55 (M55, 13 October–17 November 2002) from Curaçao/Netherlands Antilles to Douala/Cameroon (Figure 1). Seawater for underway fCO_2 measurements was drawn from a continuous seawater pumping system featuring a submersible pump located in the ship's "moon pool" at about 5 m depth. The seawater fCO_2 was measured using a seawater-air equilibrator at ambient pressure and non-dispersive infrared detection of CO_2 in the dried gas phase (see *Körtzinger* [1999], present method only slightly modified). The estimated accuracy (precision) of seawater fCO_2 measurements was ± 3 (± 0.5) μatm. In situ surface seawater temperature and salinity were measured continuously with a small CTD probe mounted at the seawater intake.

[6] The estimation of the annual CO_2 sink in the tropical Atlantic Ocean as driven by the Amazon River discharge requires climatological data for surface seawater temperature (SST) and salinity (SSS) as well as wind speed which were retrieved as monthly means from the $1° \times 1°$ World Ocean Atlas 2001 climatology (SST: *Stephens et al.*, 2002; SSS: *Boyer et al.*, 2002) and the $4° \times 4°$ COADS wind speed climatology (http://ferret.pmel.noaa.gov).

0094-8276/03/2003GL018841

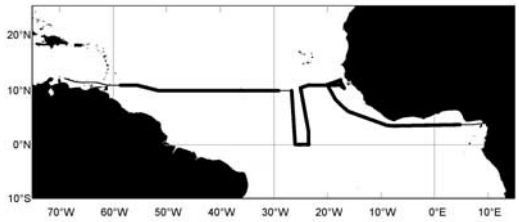

Figure 1. Track of R/V Meteor cruise 55 from Curaçao/ Netherlands Antilles to Douala/Cameroon (13 October–17 November 2002). Measurements of the CO_2 fugacity in surface seawater are available on those parts of the track marked with a bold line.

[7] The net air-sea CO_2 flux, $F_{\text{air-sea}}$ was calculated using the following bulk formula:

$$F_{\text{air-sea}} = k \cdot K_0 \cdot \left(f\text{CO}_2^{\text{air}} - f\text{CO}_2^{\text{sea}} \right) \quad (1)$$

where k is the transfer coefficient for climatological winds after *Wanninkhof* [1992], K_0 is the solubility of CO_2 in seawater after *Weiss* [1974], and $f\text{CO}_2^{\text{air}}$ and $f\text{CO}_2^{\text{sea}}$ are the CO_2 fugacities of atmospheric air and surface seawater, respectively, each given at 100% humidity and SST.

[8] All CO_2 system calculations were carried out using the software program of *Lewis and Wallace* [1998] and the carbonic acid dissociation constants after *Mehrbach et al.* [1973] (refit by *Dickson and Millero* [1987]).

3. Results and Discussion

[9] In the western half of the M55 cruise track a strong drop in surface salinity from around 35.5 ± 0.5 to less than 30 was encountered between 53°W and 51°W (Figure 2). This shallow (10–15 m) low-salinity layer was due to the Amazon River discharge. Surface seawater in the plume showed significant undersaturation with respect to atmospheric CO_2 concentrations (Figure 2) with minimum seawater $f\text{CO}_2$ values around 290 μatm. This is in stark contrast to surrounding tropical Atlantic surface waters which are typically close to or moderately above equilibrium with the atmosphere (Figure 2) [*Lefèvre et al.*, 1998; A. Körtzinger, Large and small-scale $f\text{CO}_2$ patterns in Atlantic Ocean surface waters during boreal fall, submitted to *Deep-Sea Res.*, 2003].

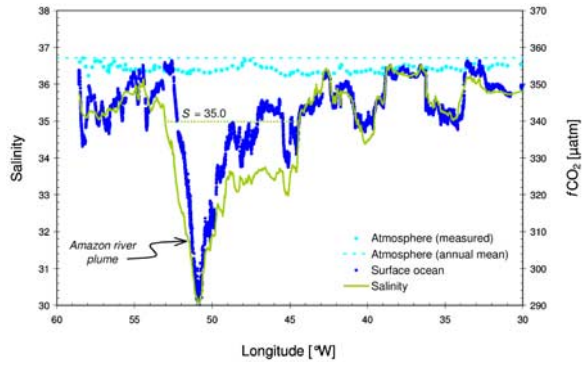

Figure 2. Measurements of CO_2 fugacity ($f\text{CO}_2$) in surface seawater and atmosphere as well as salinity in the western half of the cruise where the Amazon River plume was crossed. Also shown is the annual mean atmospheric $f\text{CO}_2$ level.

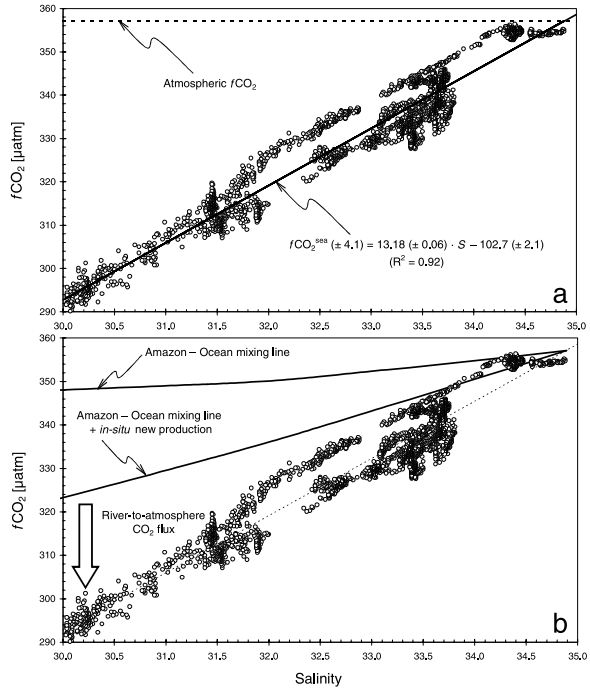

Figure 3. (a) Linear relationship between CO_2 fugacity ($f\text{CO}_2$) and salinity in surface seawater influenced by the Amazon River plume ($S < 35.0$). (b) The same relationship superimposed on the predicted $f\text{CO}_2$-S relationships for mixing alone and mixing + in situ new production.

[10] A closer inspection of the shape of the plume reveals a sharp western boundary near 52°W whereas the eastern flank is much less clearly defined. The latter is due to the retroflection of the NBC which advects plume-influenced surface waters eastward into the NECC.

[11] Waters within the Amazon River plume ($S < 35.0$) were characterized by a tight correlation between $f\text{CO}_2$ and salinity (Figure 3a). The two branches at $S > 31.5$ correspond to the two flanks of the plume. The steep western flank yields a tighter correlation but the slopes of the two branches are identical. The overall slope of 13.18 ± 0.06 is in reasonably good agreement with a slope of 11.72 ± 0.06 found by *Ternon et al.* [2000] for the wider range of 17–36 in salinity and 150–400 μatm in seawater $f\text{CO}_2$ encountered during three cruises at different seasons (Sept./Oct. 1995, April/May 1996, May 1996). This indicates that the observed $f\text{CO}_2$-S relationship is a robust feature throughout the year. The resulting salinity minimum propagates into the surface circulation of the western tropical Atlantic and reaches the NBC retroflection area (9°N, 47°W) according to the SSS climatology between August and October, i.e., about 3 months after maximum discharge.

[12] The spatial and temporal robustness of the $f\text{CO}_2$-S relationship provides a means for estimation of the annual net air-sea flux of CO_2 in the tropical Atlantic due to the Amazon River plume. Based on the M55 relationship (Figure 3a) surface seawater becomes undersaturated with respect to the annual mean atmospheric $f\text{CO}_2$ at salinities below 34.9 which I use as the upper salinity limit in the following calculation. In order to calculate the plume-

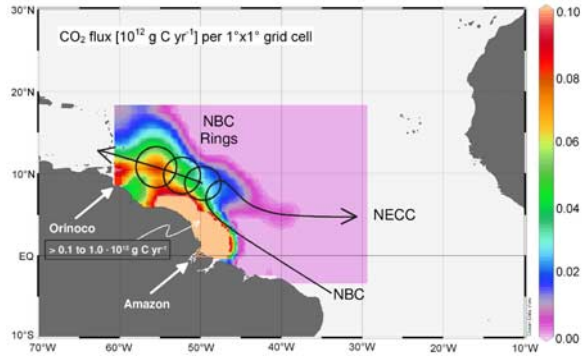

Figure 4. Annual net air-sea CO_2 flux associated with the spreading of the Amazon River plume into the tropical Atlantic Ocean.

related oceanic CO_2 sink, monthly climatological 1° × 1° SSS means (Word Ocean Atlas 2001) were converted into an air-sea fCO_2 difference (ΔfCO_2) using equation (2). This approach was restricted to grid cells with 15.0 < SSS < 34.9 in the area 3°S–18°N, 30–60°W. The lower salinity boundary is close to where observations are available from *Ternon et al.* [2000] and is regarded as a conservative limit for this extrapolation.

$$fCO_2^{air} - fCO_2^{sea} = 357.1 - (13.18 \cdot SSS - 120.7) \qquad (2)$$

[13] The plume-related ΔfCO_2 can be converted into a net air-sea CO_2 flux density using equation (1), where k and K_0 are calculated from climatological data for SST and wind speed. Multiplied by the surface area of each grid cell, this flux density yields an annual plume-related flux per grid cell (Figure 4). The resulting flux patterns are a mean representation of the propagation of the Amazon River (and to a little extent also Orinoco) waters with the surface circulation of the western tropical Atlantic. As expected, highest CO_2 fluxes are found on and near the shelf with maximum flux densities of up to 46 mmol m^{-2} d^{-1}, equaling 200 mmol m^{-2} yr^{-1} or cell fluxes of up to $1.0 \cdot 10^{12}$ g C yr^{-1}. This is in very good agreement with *Ternon et al.* [2000] who report maximum air-sea flux densities of around 40 mmol m^{-2} d^{-1} at salinities below 20 in the Amazon river plume off Cayenne/French Guiana.

[14] The total net air-sea flux into the tropical Atlantic associated with the Amazon river plume is 0.014 ± 0.005 Pg C yr^{-1} across the domain's surface area of $2.4 \cdot 10^6$ km^2. This is probably a conservative estimate as I did not include plume areas with $S < 15$, nor the westward propagation of the signal into the Caribbean. Furthermore, the sink was calculated against an equilibrium background situation. Referencing it against the mean slightly supersaturated background in the tropical Atlantic would thus increase the estimate and take into account the net effect of the Amazon River discharge on the oceanic air-sea CO_2 flux. In order to put the flux number into perspective, it is compared to the net air-sea CO_2 flux of −0.15 Pg C yr^{-1} given by *Takahashi et al.* [2002] for the eight times larger zonal band 14°N–14°S in the Atlantic sector (surface area $18.4 \cdot 10^6$ km^2). The corresponding mean air-sea CO_2 flux densities of 1.35 mmol m^{-2} d^{-1} into the plume and −1.84 mmol m^{-2} d^{-1} out of the 14°N–14°S zonal band are thus of similar magnitude but opposite sign. This illustrates that the impact of large rivers such as the Amazon is not confined to the coastal zone but can actually affect large ocean areas.

[15] On the other hand, the plume-driven oceanic CO_2 sink of 0.014 ± 0.005 Pg C yr^{-1} is more than one order of magnitude smaller than the total CO_2 source of 0.5 Pg C yr^{-1} from Amazonian rivers and wetlands [*Richey et al.*, 2002] and can therefore not offset the latter by any significant amount. The plume-driven air-sea CO_2 flux is, however, of similar magnitude as the fluvial organic and inorganic carbon exports of 0.037 and 0.035 Pg C yr^{-1}, respectively [*Richey et al.*, 1990]. The turnover and fate of these carbon inputs into the plume remain largely unclear and deserve more detailed studies.

[16] In the following, a rough back-of-the-envelope calculation is employed to explain the plume's low fCO_2 in terms of the two major driving factors: (1) Mixing between Amazon and ocean waters, and (2) in-situ biological production in the plume.

[17] (1) A 10-year time series of the chemistry of Amazon River near Manaus, Brazil, shows mean concentrations of 744 ± 126 μmol kg^{-1} for dissolved inorganic carbon (DIC) and 600 ± 115 μmol kg^{-1} for total alkalinity (A_T) [*Devol et al.*, 1995] corresponding to an fCO_2 of around 4500 μatm (at 29°C). Under these conditions, almost 20% of the DIC is in the form of dissolved CO_2(aq). When meeting the ocean, the river water is still strongly supersaturated despite strong outgassing of CO_2 but dilution with the high-alkalinity ocean endmember causes a marked drop in fCO_2. This mixing effect can be estimated by defining two endmembers: a) Amazon River water based on means from the Manaus time series (T = 29°C, S = 0, DIC = 744 μmol kg^{-1}, A_T = 600 μmol kg^{-1}, PO_4^{3-} = 0.8 μmol kg^{-1}, $SiO(OH)_3^-$ = 150 μmol kg^{-1}), and b), open ocean water at equilibrium with an atmospheric fCO_2 of 357.1 μatm (T = 29°C, S = 34.9, DIC = 1948 μmol kg^{-1}, A_T = 2306 μmol kg^{-1}, PO_4^{3-} = 0.0 μmol kg^{-1}, $SiO(OH)_3^-$ = 1.5 μmol kg^{-1}). The resulting mixing line shows fCO_2 values (minimum ~345 μatm at $S \sim 28$) significantly above measured fCO_2 (Figure 3b) indicating that net primary production in plume waters must be significant.

[18] (2) In-situ primary production in the turbid waters of the Amazon River is very low. Inorganic nutrients are thus carried to the ocean where mixing with the clear ocean waters reduces turbidity to levels which make sufficient light available for primary production. In the Amazon River plume this occurs at salinities above 7 and leads to pronounced diatoms blooms which efficiently deplete nitrate and phosphate as well as reduce silicate by about 25% across the salinity range 8–15 [*Edmond et al.*, 1981]. The concurrent net biological DIC drawdown can be estimated by employing a Redfield-type calculation. The total phosphate drawdown of 0.8 μmol kg^{-1} between Manaus and the ocean endmember was converted into a concurrent DIC drawdown by applying the C_{org}:P ratio of 123 given by *Körtzinger et al.* [2001]. The conversion yields a biologically mediated DIC change of 96 μmol kg^{-1}. Applying this DIC drawdown linearly over the salinity range 8–15 to the CO_2 system properties expected from the pure mixing line yields a fCO_2-S relationship which is closer to but still significantly larger than the actual fCO_2 measurements (Figure 3b).

[19] To resolve the remaining discrepancy, different processes have to be taken into account. The major unaccounted

process is DIC-loss from highly supersaturated river waters due to net water-to-air CO_2 flux. A proper quantitative assessment of this effect would require CO_2 system data near the river mouth or at least further downstream of Manaus. Such data is available only to a very limited extent. *Richey et al.* [1991] give a mean DIC range of 485–667 μmol dm^{-3} for Obidos, roughly halfway between Manaus and the river mouth. This represents a significant DIC loss with respect to the range near Manaus (491–1084 μmol dm^{-3}) reflecting CO_2 loss to the atmosphere. As no alkalinity values are provided for the Obidos station, a revised endmember calculation is not feasible. However, this observation clearly indicates that the river DIC endmember used in the above mixing calculation appears to be significantly overestimated. Full accounting for the DIC loss to the atmosphere would thus bring down the mixing line to lower fCO_2 values.

[20] In the respect it may be noteworthy that the river endmember in the calculation performed by *Ternon et al.* [2000] seems inappropriate. They use the same alkalinity value of 600 μmol dm^{-3}, but assume that DIC and alkalinity in the river water are equal. The corresponding fCO_2 around 450 μatm is one order of magnitude smaller than the observed fCO_2 level in the river, which accounts for almost an additional 20% in DIC. Consequently the mixing line of *Ternon et al.* [2000] must be biased strongly towards low fCO_2 values.

[21] Another possible effect unaccounted for in the present estimation is the release of phosphorus from remineralization of particulate organic matter and perhaps some remobilization of phosphorus adsorbed to suspended inorganic particles in the estuarine salinity gradient. These significant phosphorus pools [*Richey et al.*, 1991] have the potential to provide additional phosphate not included in the above calculation. For example, an underestimation of the phosphate drawdown by 0.2 μmol kg^{-1} corresponds to an overestimation of fCO_2 in the plume by more than 50 μatm (at $S = 15$).

[22] Both effects, CO_2 loss from river waters to the atmosphere and unaccounted phosphate sources, would bring fCO_2 prediction and observation more in line. Although admittedly rather crude, this estimation indicates that the observed fCO_2-S relationship in the Amazon River plume can be explained by the combined effects of CO_2 outgassing from the river water, mixing between river and ocean water, and new biological production in the river plume. A better quantitative understanding of carbon cycling in the Amazon River plume would require dedicated studies of the crucial estuarine and coastal transition zone between river and ocean waters.

4. Conclusions

[23] The Amazon River discharges on average about 0.2 Sv (1 Sv = 10^6 m^3 s^{-1}) of nutrient-rich, and CO_2-supersaturated water into the tropical Atlantic Ocean. This water becomes part of the dynamic surface circulation in the western tropical North Atlantic. Due to outgassing from the river, mixing of river and ocean waters, and net primary production, the plume waters become markedly undersaturated with respect to atmospheric CO_2. The resulting oceanic CO_2 sink is in contrast to the situation in the tropical surface waters which are typically slightly supersaturated. Calculated CO_2 flux densities are of similar magnitude and opposite sign as the typical tropical source function and illustrate the potential influence of rivers on large ocean areas.

[24] **Acknowledgments.** I thank chief scientist Douglas Wallace and Hermann Bange for perfect organization of this first German SOLAS cruise. This work was supported by the German Research Foundation through grant no. WA 1434/3.

References

Boyer, T. P., C. Stephens, J. I. Antonov, M. E. Conkright, M. A. Locarnini, T. D. O'Brien, and H. E. Garcia, World Ocean Atlas 2001, Volume 2: Salinity, edited by S. Levitus, NOAA Atlas NESDIS 50, U.S. Government Printing Office, Wash., D. C., 165 pp., CD-ROMs, 2002.

Cole, J. J., and N. F. Caraco, Carbon in catchments: Connecting terrestrial carbon losses with aquatic metabolism, *Mar. Freshwater Res.*, *52*, 101–110, 2001.

Devol, A. H., B. R. Forsberg, J. E. Richey, and T. P. Pimentel, Seasonal variation in chemical distributions in the Amazon (Solimões) River: A multiyear time series, *Global Biogeochem. Cycles*, *9*, 307–328, 1995.

Dickson, A. G., and F. J. Millero, A comparison of the equilibrium constants for the dissociation constants of carbonic acid in seawater media, *Deep Sea Res.*, *34*, 1733–1743, 1987.

Edmond, J. M., E. A. Boyle, B. Grant, and R. F. Stallard, Chemical mass balance in the Amazon plume I: The nutrients, *Deep Sea Res.*, *28*, 1339–1374, 1981.

Fratantoni, D. M., and D. A. Glickson, North Brazil Current ring generation and evolution observed with SeaWIFS, *J. Phys. Oceanogr.*, *32*, 1058–1074, 2002.

Körtzinger, A., Determination of carbon dioxide partial pressure ($p(CO_2)$), in *Methods of Seawater Analysis*, edited by K. Grasshoff, K. Kremling, and M. Ehrhardt, pp. 149–158, Verlag Chemie, Weinheim, 1999.

Körtzinger, A., J. I. Hedges, and P. D. Quay, Redfield ratios revisited: Removing the biasing effect of anthropogenic CO_2, *Limnol. Oceanogr.*, *46*, 964–970, 2001.

Lefèvre, N., G. Moore, J. Aiken, A. J. Watson, D. J. Cooper, and R. Ling, Variability of pCO_2 in the tropical Atlantic in 1995, *J. Geophys. Res.*, *103*, 5623–5634, 1998.

Lewis, E., and D. W. R. Wallace, Program developed for CO_2 system calculations, Carbon Dioxide Information Analysis Center, Report ORNL/CDIAC-105, Oak Ridge National Laboratory, Oak Ridge, TN, 1998.

Mehrbach, C., C. H. Culberson, J. E. Hawley, and R. M. Pytkowicz, Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, *18*, 897–907, 1973.

Richey, J. E., J. I. Hedges, A. H. Devol, P. D. Quay, R. Victoria, L. Martinelli, and B. R. Forsberg, Biogeochemistry of carbon in the Amazon River, *Limnol. Oceanogr.*, *35*, 352–371, 1990.

Richey, J. E., R. L. Victoria, E. Salati, and B. R. Forsberg, The Biogeochemistry of a Major River System: The Amazon Case Study, in *Transport of Carbon and Minerals in Major World Rivers*, edited by E. T. Degens, S. Kempe, and J. E. Richey, pp. 57–74, Wiley and Sons, New York, 1991.

Richey, J. E., J. M. Melack, A. K. Aufdenkampe, V. M. Ballester, and L. L. Hess, Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2, *Nature*, *416*, 617–620, 2002.

Stephens, C., J. I. Antonov, T. P. Boyer, M. E. Conkright, R. A. Locarnini, T. D. O'Brien, and H. E. Garcia, World Ocean Atlas 2001, Volume 1: Temperature, edited by S. Levitus, NOAA Atlas NESDIS 49, U.S. Government Printing Office, Wash., D. C., 167 pp., CD-ROMs, 2002.

Takahashi, T., S. C. Sutherland, C. Sweeney, A. Poisson, N. Metzl, B. Tilbrook, N. Bates, R. Wanninkhof, R. A. Feely, C. Sabine, J. Olafsson, and Y. Nojiri, Global air-sea CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects, *Deep Sea Res. II*, *49*, 1601–1622, 2002.

Ternon, J. F., C. Oudot, A. Dessier, and D. Diverres, A seasonal tropical sink for atmospheric CO_2 in the Atlantic ocean: The role of the Amazon River discharge, *Mar. Chem.*, *68*, 183–201, 2000.

Wanninkhof, R., Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, *97*, 7373–7382, 1992.

Weiss, R. F., Carbon dioxide in water and seawater: The solubility of a non-ideal gas, *Mar. Chem.*, *2*, 203–215, 1974.

A. Körtzinger, Institut für Meereskunde, Universität Kiel, Düsternbrooker Weg 20, D-24105, Kiel, Germany. (akoertzinger@ifm.uni-kiel.de)